

# PATENT SPECIFICATION

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NO DRAWINGS.

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## COMPLETE SPECIFICATION.

### Non-Ionic Detergent Compositions.

We, BRITISH NYLON SPINNERS LIMITED, of Pontypool, Monmouthshire, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to detergent compositions for textiles comprising a non-ionic surface active agent and more particularly to such detergents wherein the non-ionic surface active agent is associated in prescribed proportions with an anionic surface active agent and with a cationic surface active agent.

These detergent compositions, although of general utility, are especially intended for use with textiles made of hydrophobic synthetic fibres, for example, nylon. These fibres are apt to become electrostatically charged and there is considerable evidence which associates much of the soiling occurring in use, with such charges. The effectiveness of the present detergent compositions accordingly appears to be largely ascribable to the cationic agent which is present in stoichiometrical excess over the anionic agent and has an antistatic influence. The cationic agent itself seems to be made resistant to rinsing by the anionic agent with which it forms a complex. It is thought that this resistance to rinsing is due to the complex having an affinity for the hydrophobic fibres ; the complex may well also act as an anti-redeposition agent. However, whether the foregoing theory be correct or not, the usefulness of the invention is in no wise dependent thereon. The scouring action of these detergents in aqueous solution is good

and the antistatic effect withstands repeated rinsing.

In the Specification of British Patent No. 641,297 there is claimed germicidal detergent compositions comprising an organic anionic detergent, an organic cationic germicide and a water soluble non-ionic surface active agent, the anionic detergent and cationic germicide being present in the relative proportions by weight of 1 : 4 to 12 : 1 and the non-ionic surface active agent being present in an amount equal to at least substantially 10% of the combined weights of the anionic and cationic agents. In general the ratio of the non-ionic agent to the combined weight of the ionic agents is within the range 1 : 9 to 1 : 1 and preferably within the range of 1 : 9 to 2 : 3. However, we have found that by a careful selection of the proportions of the anionic, cationic and non-ionic surface active agents, in particular by using a stoichiometric excess of the cationic surface active agent over the anionic surface active agent and an amount of non-ionic surface active agent such that it constitutes more than 50% by weight of the total surface active agents, we obtain detergent compositions which, when used in washing textiles made of hydrophobic fibres, surprisingly, confer antistatic character to said textiles.

The non-ionic surface active agents to be employed are defined hereinafter and in the appending claims by the following expressions, namely, non-ionic organic water-soluble compounds comprising a hydrocarbon radical derivable from natural fats or from petroleum or an alkylaryl radical derivable from natural fats or from petroleum or an alkylaryl radical as the hydrophobic or

lipophilic portion and a polyhydroxy or polyoxyalkylene residue as the hydrophilic portion. Whilst not strictly non-ionic, the ionising power of these compounds is negligible compared with that of the anionic and cationic surface active agents. The anionic surface active agents are water-soluble compounds having lipophilic and hydrophilic groups in their anion, whereas the cationic surface active agents have lipophilic and hydrophilic groups in their cation (cf. pages 108 and 109 of "Surface Active Agents" by C. B. F. Young and K. W. Carns, 1945, Chemical Publishing Co. Inc.).

In the manufacture of the present detergent compositions the anionic and cationic surface active agents may be added to the non-ionic surface active agent separately or in the form of their complexes. The latter, as is well-known, are insoluble in water, being precipitated when aqueous solutions of the anionic and cationic agents are mixed in stoichiometrical proportion. The complexes are, however, peptised or solubilised by an excess of either the anionic or cationic agent in aqueous solution; the complexes also dissolve in aqueous solutions of non-ionic surface active agents. Consequently, when the detergent compositions of this invention are made use of by dissolving them in water, no troublesome precipitate of the complex is formed.

The mixtures of non-ionic, anionic and cationic surface active agents of this invention may be liquid or solid, but it is preferred that they be liquid at room temperature or at least liquefiable by warming to 90° C. because they are usually found to disperse or dissolve more readily in water when liquid. Instead of warming, a suitable solvent may optionally be incorporated in the mixtures to form a liquid solution. In this connection it may be added that the surface active ingredients of the present detergent compositions, some of which are solid, some semi-solid and some liquid, when in the pure state, are commonly marketed commercially in the form of liquid solutions.

Accordingly the invention relates to intimate mixtures or solutions, comprising a non-ionic surface active agent as hereinbefore defined, an anionic surface active agent and a cationic surface active agent, and optionally including a solvent therefor, characterised in that the non-ionic surface active agent constitutes from 51% to 98½%, the cationic surface active agent from 1% to 48½% and the anionic surface active agent from ½% to 24% of the total surface active agents, and that the cationic surface active agent is always present in stoichiometrical excess over the anionic surface active agent.

Preferably the non-ionic surface active agent constitutes at least 80% of the total surface active agents, the cationic surface

active agent from 1% to 11% thereof and the anionic surface active agent from ½% to 9% thereof. All parts, percentages and proportions in the Specification and claims are to be taken by weight unless otherwise specified.

Examples of the surface active agents, which may be employed are given below. It will be understood that a plurality of any or each of the surface active agents may be used. Indeed the commercially available agents often consist of mixtures of several compounds, usually of closely related chemical structure.

#### *Non-ionic Surface Active Agents.*

*p*-Dodecylphenyl polyethylene glycol ether 80  
 9 : 9 : 9-Trimethylnonyl polyethylene glycol ether  
*p*-1 : 1 : 3 : 3-Tetramethylbutylphenyl polyethylene glycol ether 75  
 Dodecyl polyethylene glycol thioether 85  
 Polyethylene glycol oleate

#### *Anionic Surface Active Agents.*

Sodium 2-ethyl-2-butylethyl sulphate  
 Sodium 2-ethyl-2-butylethyl phosphate  
 Sodium 3-ethyl-3-butylpropyl-3<sup>1</sup> : 3<sup>1</sup> 90  
     diethylpropyl-methyl sulphate  
 Sodium 3-ethyl-3-butyl propyl-3<sup>1</sup> : 3<sup>1</sup>  
     dimethylpropyl-methyl sulphate  
 Sodium oleyl sulphate  
 Sodium dodecyl sulphate 95  
 Sodium 1-ethyldodecyl sulphate  
 Sodium 1-ethyltridecyl sulphate  
 Sodium *p*-dodecylbenzene sulphonate  
 Oleoyl methyl taurine  
 Sodium isopropyl naphthalene sulphonate 100  
 Sodium oleate

#### *Cationic Surface Active Agents.*

Hexadecyl pyridinium chloride  
 Dodecyl pyridinium chloride  
 Didecyltrimethylammonium bromide 105  
 Didodecyltrimethylammonium bromide  
 Stearyltrimethylbenzylammonium chloride  
 Benzyltri (dimethylamino) phosphonium chloride  
 Hexadecyltrimethylammonium chloride 110  
 Octadecyltrimethylammonium chloride  
 Octadecenyltrimethylammonium chloride  
 Octadecadienyltrimethylammonium chloride

The surface active ingredients of the present detergent compositions may be mixed in any convenient manner. If they are solid or waxy they may be melted together. If they are already in solution, they can be simply stirred together. The commercially available surface active agents which are already in solution as marketed are thus easy to mix. In any case it is preferred that the mixed surface active agents of these detergents be in liquid or liquefiable form, and various solvents may be added, when

necessary, to dissolve the active agents. The following solvents are quoted as examples :—

- 5 water  
methyl alcohol  
ethyl alcohol  
trichloroethylene  
carbon tetrachloride  
decahydronaphthalene  
10 benzene  
glycerol  
ethylene glycol  
hexylene glycol  
isopropyl alcohol

15 It is sometimes found that concentrated aqueous solutions of the mixed non-ionic and cationic surface active agents are cloudy and/or viscous. Such solutions can be rendered clear and free flowing by the addition of further solvents, e.g. one of those in the above list.

The following examples are intended to illustrate but not limit, the present invention.

The surface active agents employed in Examples 1, 2, 3, 4 and 5 are :—

- 25 (1) *Non-ionic surface active agent* :—  
25% aqueous solution of *p*-dodecyl-phenyl polyethylene glycol ether containing 17 ethylene glycol residues.  
30 (2) *Anionic surface active agent* :—  
30% aqueous solution of sodium 1-ethyl-tridecyl sulphate.  
(3) *Cationic surface active agent* :—  
50% isopropanolic solution of a mixture of equal parts of octadecadienyltrimethylammonium chloride and octadecenyl-trimethylammonium chloride.

N.B. The percentages are calculated with respect to the solutions.

#### EXAMPLE 1.

The detergent composition is made by mixing the above three solutions in the following proportions by volume :—

- (1) Solution of non-ionic agent 98 parts  
(2) Solution of anionic agent 1 part  
(3) Solution of cationic agent 1 part 45

This mixture constitutes a detergent composition of the present invention.

A plain weave fabric of 30 denier nylon yarn (10 filaments) is washed repeatedly and examined as to its tendency to become electrostatically charged in the following manner :—

The fabric, divided into 15 strips, is immersed and agitated for 3 minutes, in 100 times its own weight of a 0.1% aqueous solution of the above detergent at 60° C. The fabric strips are then removed, rinsed once with warm water and twice with cold water, and dried. One strip is set aside and the remaining fourteen washed again, rinsed and dried as before. Another strip is set aside and the process repeated until the final strip has received 15 washes.

The strips of fabric are stored for 24 hours in an atmosphere of 65% relative humidity at 21° C. together with 22 strips of the same fabric which have not been washed. Each strip measuring 4" × 1½" is then tested as follows. The fabric is placed on filter paper, is brushed 3 times with a nylon brush and put into the inner container of a Faraday Ice Pail. The charge produced, in a circuit of constant capacity, is read in terms of voltage from a Rothschild Electrostatic Voltmeter (obtainable from Messrs. Rothschild of Waffenplatz, Zurich), the following results being obtained :—

No. of washes	1	2	3	4	5	6	7	8	9	10
Voltage	0	0	-10	0	+10	+30	+10	+60	+50	+80

No. of washes	11	12	13	14	15
Voltage	-20	+30	-50	-10	-60

Mean voltage is therefore (irrespective of sign)

28 volts

Unwashed fabric (mean of 22 tests)

114 volts

85 The following four examples are carried out in exactly the same way as Example 1, except that only 10 washes are given. The results of the tests are quoted in the following table.

TABLE 1.

Example		2	3	4
5	Non-ionic agent solution	91 parts	98½ parts	96 parts
	Anionic agent solution	2½ parts	½ part	1 part
	Cationic agent solution	6½ parts	1 part	3 parts
		(all parts being parts by volume)		
		Voltage		
10	No. of washes			
	1	+15	0	0
	2	0	+15	-10
	3	+30	+30	+10
	4	+10	+20	-65
	5	0	+10	-20
15	6	+10	+25	+10
	7	0	0	+15
	8	+10	+10	+50
	9	0	-10	+25
	10	+20	-10	+10
Mean (irrespective of sign)		10	13	22
20	Unwashed fabric	185	77	114
		(mean of 22 results)	(mean of 19 results)	(mean of 22 results)

## EXAMPLE 5.

This example is performed in the same way as Example I, the surface active agents being

employed in the following proportions (N.B. the proportions of pure active agent as percentages are quoted in brackets).

30	Non-ionic agent solution	81½ parts by volume	(70.8%)
	Anionic agent solution	4 "	( 4.2%)
	Cationic agent solution	14½ "	(25.0%)
			100.0%

The results of the tests are :—

		No. of washes	Voltage
35		1	+30
		2	0
		3	0
		4	0
		5	0
		6	0
40		7	0
		8	0
		9	0
		10	0
45	Mean		3
	(irrespective of sign)		
Unwashed fabric			185
(mean result)			

The figures below illustrate clearly the inferior electrostatic results obtained when the proportions of surface active agents prescribed by the invention are departed from:—

5	Example	Proportions of pure active agents employed expressed as percentages.			Mean Voltage
		Non-ionic	Anionic	Cationic	
	1	96.7%	1.2%	2.1%	28
	2	84.8%	2.7%	12.5%	10
	3	96.4%	0.6%	2.0%	13
10	4	92.6%	1.4%	6.0%	22
	5	70.8%	4.2%	25.0%	3
	—	78.0%	14.7%	7.3%	56
	—	0	100.0%	0	86
	—	80.8%	19.2%	0	55
15	—	44.8%	46.7%	8.5%	30
	—	11.7%	0	88.3%	26

Although it is possible to obtain satisfactory electrostatic tests by increasing the proportion of cationic surface active agent, as shown by the last row of fibres quoted above, such mixtures, apart from the greater cost thereof, tend to possess inadequate detergency powers.

Other examples of the present detergents are given below.

#### EXAMPLE 6.

53 Parts of Nonionic XD (a soft solid polyalkylene glycol ether obtainable from the Union Carbide Chemicals Company) are mixed with 20 parts of a 25% aqueous solution of sodium 3-ethyl-3-butylpropyl-3<sup>1</sup>:3<sup>1</sup>-diethylpropyl-methyl sulphate. The mixture is melted by warming to 50° C., and 84 parts of a 50% aqueous paste of stearyl dimethylbenzylammonium chloride are added and the whole stirred together. The proportions of pure active agents in the resulting detergent composition are:—

Non-ionic agent	53%
Anionic agent	5%
Cationic agent	42%
	100%

#### EXAMPLE 7.

53 Parts of Nonionic XD are melted with 35 parts of a 40% aqueous solution of sodium 2-ethyl-2-butylethyl sulphate by warming to 50° C. 33 Parts of hexadecyl pyridinium chloride are added with stirring. The proportions of pure active agents in the resulting detergent composition are:—

Non-ionic agent	53%
Anionic agent	14%
Cationic agent	33%
	100%

#### EXAMPLE 8.

19 Parts of sodium *p*-dodecylbenzene sulphonate are dissolved in 200 parts of water and the resulting solution mixed with a solution of 28 parts of hexadecyl pyridinium chloride in 300 parts of water. A precipitate is thrown down, but redissolves on the addition of 53 parts of Nonionic NPX (an alkyl-phenyl polyethylene glycol ether obtainable from the Union Carbide Chemicals Company). The proportions of pure active agents in the resulting detergent composition are:—

Non-ionic	53%
Anionic	19%
Cationic	28%
	100%

#### EXAMPLE 9.

260 Parts of a 25% aqueous solution of *p*-dodecylphenyl polyethylene glycol ether (containing 17 ethylene glycol residues) are mixed with 14 parts of sodium oleate and 21 parts of dodecyl pyridinium chloride. The proportions of pure active agents in the resulting detergent composition are:—

Non-ionic	65%
Anionic	14%
Cationic	21%
	100%

#### EXAMPLE 10.

65 Parts of Nonionic NP35 (an alkyl-phenyl polyethylene glycol ether obtainable from the Union Carbide Chemicals Company) are melted at 50° C. To this melt 35 parts of an 80% aqueous gel of didecyl dimethylammonium bromide are added. The resulting mixture is stirred with 17½ parts of a 40% aqueous solution of sodium 2-ethyl-2-butylethyl sulphate. The proportions of

pure active agents in the resulting detergent composition are :—

5	Non-ionic	65%
	Anionic	7%
	Cationic	28%
		100%

#### EXAMPLE 11.

72½ Parts of a 90% aqueous solution of 9 : 9 : 9-trimethylnonyl polyethylene glycol ether are mixed with 31 parts of dodecyl pyridinium chloride and 16 parts of a 25% aqueous solution of sodium 2-ethyl-2-butyl-ethyl phosphate. The proportions of pure active agents in the resulting detergent composition are :—

Non-ionic	65%
Anionic	4%
Cationic	31%
	100%

#### EXAMPLE 12.

75 Parts of Nonionic NP40 (an alkylphenyl polyethylene glycol ether obtainable from the Union Carbide Chemicals Company) are mixed with 33 parts of a 30% aqueous solution of sodium 1-ethyltridecyl sulphate and 18½ parts of an 80% aqueous paste of didecyl-dimethylammonium bromide. The proportions of pure active agents in the resulting detergent composition are :—

Non-ionic	75%
Anionic	10%
Cationic	15%
	100%

#### EXAMPLE 13.

75 Parts of Nonionic XH (a polyalkylene glycol ether obtainable from the Union Carbide Chemicals Company) are dissolved in 200 parts of carbon tetrachloride and mixed with 24 parts of a 25% aqueous solution of sodium 3-ethyl-3-butylpropyl-3<sup>1</sup>:3<sup>1</sup>-dimethylpropyl-methyl sulphate. 19 Parts of dodecyl pyridinium chloride are added to the mixture. The proportions of pure active agents in the resulting detergent composition are :—

Non-ionic	75%
Anionic	6%
Cationic	19%
	100%

#### EXAMPLE 14.

21 Parts of dodecyl pyridinium chloride are dissolved in 100 parts of methyl alcohol and the resulting solution added to 83 parts

of a 90% aqueous solution of 9 : 9 : 9-trimethylnonyl polyethylene glycol ether. To the mixture so-obtained 4 parts of sodium oleate are added. The proportions of pure active agents in the resulting detergent composition are :—

Non-ionic	75%
Anionic	4%
Cationic	21%
	100%

#### EXAMPLE 15.

To 80 Parts of Nonionic NP27 (an alkyl-phenyl polyethylene glycol ether obtainable from the Union Carbide Chemicals Company) are added 14 parts of dodecyl pyridinium chloride and 6 parts of sodium dodecyl sulphate. The proportions of pure active agents in the resulting detergent composition are :—

Non-ionic	80%
Anionic	6%
Cationic	14%
	100%

#### EXAMPLE 16.

To 352 parts of a 25% aqueous solution of *p*-dodecylphenyl polyethylene glycol ether (containing 17 ethylene glycol residues) are added 11.2 parts of an 80% aqueous gel of didecyl-dimethylammonium bromide and 3 parts of sodium *p*-dodecylbenzene sulphonate. The proportions of pure active agents in the resulting detergent composition are :—

Non-ionic	88%
Anionic	3%
Cationic	9%
	100%

#### EXAMPLE 17.

95 Parts of Nonionic XD are dissolved in 200 parts of isopropanol ; 13 parts of hexadecyl pyridinium chloride are added to the resulting solution, followed by 2 parts of sodium oleate. The proportions of pure active agents in the resulting detergent composition are :—

Non-ionic	95%
Anionic	2%
Cationic	13%
	100%

#### WHAT WE CLAIM IS :—

1. Detergent compositions adapted to confer antistatic character to textiles made from hydrophobic fibres when used in washing said textiles, comprising intimate mix-

tures or solutions of a non-ionic surface active agent as hereinbefore defined, an anionic surface active agent, and a cationic surface active agent, and optionally including a solvent therefore, characterised in that the non-ionic surface active agent constitutes from 51% to 98½%, the cationic surface active agent from 1% to 48½% and the anionic surface active agent from ½% to 24% of the total surface active agents, and that the cationic surface active agent is always present in stoichiometrical excess over the anionic surface active agent.

2. Detergent compositions, as claimed in Claim 1 wherein the non-ionic surface active agent constitutes from 80% to 98½%, the cationic surface active agent from 1% to 11%, and the anionic surface active agent from ½% to 9% of the total surface active agents.

3. Detergent compositions, as hereinbefore described, with particular reference to the foregoing examples.

S. CLARK,  
Chartered Patent Agent.

#### PROVISIONAL SPECIFICATION.

#### Non-Ionic Detergent Compositions.

We, BRITISH NYLON SPINNERS LIMITED, of Pontypool, Monmouthshire, a British Company, do hereby declare this invention to be described in the following statement:—

This invention relates to detergents for textiles comprising a non-ionic surface active agent and more particularly to such detergents wherein the non-ionic surface active agent is associated with an anionic surface active agent and with a cationic surface active agent.

These detergents, although of general utility, are especially intended for use with textiles made of hydrophobic synthetic fibres, for example, nylon. These fibres are apt to become electrostatically charged and there is considerable evidence which associates much of the soiling occurring in use, with such charges. The effectiveness of the present detergents accordingly appears to be largely ascribable to the presence of the cationic agent which has an antistatic influence. The cationic agent itself seems to be made resistant to rinsing by the anionic agent with which it forms a complex. It is thought that this resistance to rinsing is due to the complex having an affinity for the hydrophobic fibres; the complex may well also act as an anti-redeposition agent. However, whether the foregoing theory be correct or not, the usefulness of the invention is in no wise dependent thereon. The scouring action of these detergents in aqueous solution is good and the antistatic effect withstands repeated rinsing.

The non-ionic surface active agents to be employed are defined by the following expression, namely, non-ionic organic water-soluble compounds comprising a hydrocarbon radical derivable from natural fats or from petroleum or an alkylaryl radical as the hydrophobic or lipophilic portion and a polyhydroxy or polyoxyalkylene residue as the hydrophilic portion. Whilst not strictly

non-ionic, the ionising power of these compounds is negligible compared with that of the anionic and cationic surface active agents. The anionic surface active agents are water-soluble compounds having lipophilic and hydrophilic groups in their anion, whereas the cationic surface active agents have lipophilic and hydrophilic groups in their cation (cf. pages 108 and 109 of "Surface Active Agents" by C. B. F. Young and K. W. Carns, 1945, Chemical Publishing Co. Inc.).

In the manufacture of the present detergents the anionic and cationic surface active agents may be added to the non-ionic surface active agent separately or in the form of their complexes. The latter, as is well-known, are insoluble in water, being precipitated when aqueous solutions of the anionic and cationic agents are mixed in stoichiometrical proportion. The complexes are, however, peptised or solubilised by an excess of either the anionic or cationic agent in aqueous solution; the complexes also dissolve in aqueous solutions of non-ionic surface active agents. Consequently when the detergents of this invention are made use of by dissolving them in water, no troublesome precipitate of the complex is formed.

The mixtures of non-ionic, anionic and cationic surface active agents of this invention may be liquid or solid, but it is preferred that they be liquid at room temperature or at least liquefiable by warming to 90° C. because they are usually found to disperse or dissolve more readily in water when liquid. Instead of warming, a suitable solvent may optionally be incorporated in the mixtures to form a liquid solution. In this connection it may be added that the surface active ingredients of the present detergents, some of which are solid some semi-solid and some liquid, when in the pure state, are commonly marketed commercially in the form of liquid solutions.

Accordingly the invention relates to intimate mixtures or solutions, comprising a non-ionic surface active agent, an anionic surface active agent and a cationic surface active agent, and optionally including a solvent therefor.

Examples of the surface active agents, which may be employed are given below. It will be understood that a plurality of any or each of the surface active agents may be used. Indeed the commercially available agents often consist of mixtures of several compounds, usually of closely related chemical structure.

15 *Non-ionic Surface Active Agents.*

*p*-Dodecylphenyl polyethylene glycol ether  
9 : 9 : 9-Trimethylnonyl polyethylene glycol ether

20 *p*-1 : 1 : 3 : 3-Tetramethylbutylphenyl polyethylene glycol ether  
Dodecyl polyethylene glycol thioether  
Polyethylene glycol oleate

*Anionic Surface Active Agents.*

25 Sodium 2-ethyl-2-butylethyl sulphate  
Sodium 2-ethyl-2-butylethyl phosphate  
Sodium 3-ethyl-3-butylpropyl-2 : 3-di-ethylpropyl-methyl sulphate  
Sodium oleyl sulphate  
Sodium dodecyl sulphate  
30 Sodium 1-ethyldodecyl sulphate  
Sodium *p*-dodecylbenzene sulphonate  
Oleoyl methyl taurine  
Sodium isopropyl naphthalene sulphate  
Sodium oleate

35 *Cationic Surface Active Agents.*

Hexadecyl pyridinium chloride  
Dodecyl pyridinium chloride  
Didodecyltrimethylammonium bromide  
Stearyltrimethylbenzylammonium chloride  
40 Benzyltri (dimethylamino) phosphonium chloride  
Hexadecyltrimethylammonium chloride  
Octadecyltrimethylammonium chloride  
Octadecenyltrimethylammonium chloride  
45 Octadecadienyltrimethylammonium chloride

The surface active ingredients of the present detergents may be mixed in any convenient manner. If they are solid or waxy they may be melted together. If they are already in solution, they can be simply stirred together. The commercially available surface active agents which are already in solution as marketed are thus easy to mix.  
55 In any case it is preferred that the mixed surface active agents of these detergents be in liquid or liquefiable form, and various solvents may be added, when necessary, to dissolve the active agents. The following solvents are quoted as examples :—

water  
methyl alcohol  
ethyl alcohol  
trichloroethylene  
carbon tetrachloride  
decahydronaphthalene  
benzene  
glycerol  
ethylene glycol  
hexylene glycol  
isopropyl alcohol

65

70

It is sometimes found that concentrated aqueous solutions of the mixed non-ionic and cationic surface active agents are cloudy and/or viscous. Such solutions can be rendered clear and free flowing by the addition of further solvents, e.g. one of those in the above list.

75

Very useful detergents according to the present invention are predominantly non-ionic, comprising (calculated on the total pure surface active agents) at least 90% of non-ionic surface active agent. Advantageously the composition may be 99.9—95% of non-ionic surface active agent, the balance of 0.1—5% consisting of stoichiometrically equal amounts of anionic surface active agents and cationic surface active agents, which latter may be introduced into the mixture either separately or in the form of their complex. As already indicated above it is usually convenient to handle the surface active agents in the form of their solutions.

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The present detergents may also advantageously comprise relatively large proportions of non-ionic and anionic surface active agents totalling (calculated on the total pure surface active agents) at least 95%, and each amounting to at least 10%, the balance of cationic agent being only sufficient to constitute, together with its stoichiometric equivalent of the anionic component agent, 0.1—5% of the total pure surface active agents. Such a detergent may be regarded as a mixture of non-ionic and anionic surface active agents containing a small amount of anionic/cationic complex.

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In yet another preferred mode of working, the non-ionic and cationic agents may be included in large proportions, each amounting to at least 10% of the total pure surface active agents and both totalling at least 95% of the whole, the balance being a relatively small proportion of anionic surface active agent sufficient to form with a little of the cationic surface active agent an anionic/cationic complex amounting to 0.1—5% of the whole.

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The above three types of mixed detergent (ignoring any solvents that may be employed) can be tabulated, assuming the theory of complex formation, as follows :—

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	Percentage* of surface active agent			Percentage* of Complex
	Anionic	Non-ionic	Cationic	
5	a little	99.9—95%	a little	0.1—5%
	total at least 95%		a little	0.1—5%
	a little	total at least 95%		0.1—5%

\* Calculated on total pure surface active agents.

The following examples, in which the parts are by volume, are intended to illustrate but not limit, the present invention.

Surface active agents employed are :—

- (1) *Non-ionic surface active agent* :—  
25% aqueous solution of *p*-dodecyl-phenyl polyethylene glycol ether containing 17 ethylene glycol residues.
  - (2) *Anionic surface active agent* :—  
30% aqueous solution of sodium 1-ethyltridecyl sulphate.
  - (3) *Cationic surface active agent* :—  
50% isopropanolic solution of a mixture of equal parts of octadecadienyltrimethylammonium chloride and octadecenyltrimethylammonium chloride.
- N.B. The percentages which are by weight are calculated with respect to the solutions.

#### EXAMPLE 1.

The detergent is made by mixing the above three solutions in the following proportions :—

- (1) Solution of non-ionic agent 98 parts
- (2) Solution of anionic agent 1 part
- (3) Solution of cationic agent 1 part

This mixture constitutes a detergent of the present invention.

A plain weave fabric of 30 denier nylon yarn (10 filaments) is washed repeatedly and examined as to its tendency to become electrostatically charged in the following manner :—

The fabric, divided into 15 strips, is immersed and agitated for 3 minutes, in 100 times its own weight of a 0.1% aqueous solution of the above detergent at 60° C. The fabric strips are then removed, rinsed once with warm water and twice with cold water and dried. One strip is set aside and the remaining fourteen washed again, rinsed and dried as before. Another strip is set aside and the process repeated until the final strip has received 15 washes.

The strips of fabric are stored for 24 hours in an atmosphere of 65% relative humidity at 21° C. together with 22 strips of the same fabric which have not been washed. Each strip measuring 4" × 1½" is then tested as follows. The fabric is placed on filter paper, is brushed 3 times with a nylon brush and put into the inner container of a Faraday Ice Pail. The charge produced, in a circuit of constant capacity, is read in terms of voltage from a Rothschild Electrostatic Voltmeter (obtainable from Messrs. Rothschild of Waffenzplatz, Zurich), the following results being obtained :—

No. of washes	1	2	3	4	5	6	7	8	9	10
Voltage	0	0	-10	0	+10	+30	+10	+60	+50	+80
No. of washes	11	12	13	14	15					
Voltage	-20	+30	-50	-10	-60					

70

Unwashed fabric (mean of 22 tests)

114 volts

The following four examples are carried out in exactly the same way as Example 1, except that only 10 washes are given. The results of the tests are quoted in the following table :—

TABLE 1.

	Example	Voltage			
		2	3	4	5
5	Non-ionic agent	97 parts	98½ parts	96 parts	91 parts
	Anionic agent	1 part	½ part	1 part	6 parts
	Cationic agent	2 parts	1 part	3 parts	3 parts
10	No. of washes				
	1	+40	0	0	0
	2	+10	+15	-10	+15
	3	+30	+30	+10	+15
	4	+30	+20	-65	+30
	5	+40	+10	-20	+25
	6	0	+25	+10	+15
	7	+70	0	+15	0
	8	+40	+10	+50	0
	9	+50	-10	+25	+10
	10	+30	-10	+10	0
20	Unwashed fabric	114	77	114	77
		(mean of 22 results)	(mean of 19 results)	(mean of 22 results)	(mean of 19 results)

## EXAMPLE 6.

The detergent is made by mixing the three solutions used in the above example in the following proportions :—

- 25 (1) Solution of non-ionic agent 15 parts  
 (2) Solution of anionic agent 46 parts  
 (3) Solution of cationic agent 39 parts

30 Nylon fabric washed once with even a 0.02% aqueous solution of this detergent, as described in Example 1, receives an anti-static effect which is not removed by the

rinsing. Thus after the washing and three rinses, once with warm water and twice with cold water, the charge produced by the electrostatic test, carried out as described above is found to be +10 volts, and on repeating the experiment, +30 volts, whereas the charge produced on the unwashed fabric is -136 volts (mean of 10 tests).

The following three examples of the present detergents are similarly effective in reducing the tendency of the fabric to become electrostatically charged :—

45	Example	Composition of Detergent		
		Non-ionic solution	Anionic solution	Cationic solution
	7	15 parts	44 parts	41 parts
	8	50 parts	35 parts	15 parts
	9	50 parts	20 parts	30 parts

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